

FEDERAL REPUBLIC OF GERMANY
GERMAN PATENT OFFICE
PATENT NO: 41 14 134 A1
Offenlegungsschrift

Int. Cl.³: D 21 C 9/16
Application No.: P 41 14 134.2
Filing Date: April 30, 1991
Laid Open to Public Inspection: November 5, 1992

METHOD FOR THE CHLORINE-FREE BLEACHING
AND DELIGNIFICATION OF ALKALI PULP

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Publications taken into consideration for the evaluation of patentability:

German Patent No. 30 05 947 B1
German Patent No. 22 19 505 [Offenlegungsschrift]
Austrian Patent No. 3 78 016
French Patent No. 8 60 112
British Patent No. 6 01 292
US Patent No. 24 42 332
European Patent No. 02 26 114 A1
Baily, C. W.:
Dence, C. W.: Peroxyacetic Acid Bleaching of Chemical
Pulps. In: TAPPI, Vol. 49, No. 1, 1966, pp. 9-15.

Method for the chlorine-free bleaching and delignification of alkali pulp

A method for the chlorine-free bleaching and delignification of alkali pulp is described, wherein the alkali pulp is subjected to a bleaching sequence, consisting of the stages:

(A) - (C) - (A) - (B) - (B)

wherein (A) = treatment with an aqueous solution of an organic per-acid, (B) = bleaching with an alkaline, aqueous peroxide solution, perhaps activated by cyanamide or cyanamide salts, and (C) = extraction of the lignin components with an alkaline aqueous solution.

In this manner, one obtains, with a relatively few bleaching stages and without using chlorine-containing chemicals, a highly bleached alkali pulp, which exhibits a brightness between 85 and 92% and a kappa value of 0.5 to 2.5.

Description

The invention under consideration concerns a method for the chlorine-free bleaching and delignification of alkali pulp.

For the preparation of brightness-stable paper products, a pulp with the lowest possible lignin content is required. For this purpose, cellulose-containing raw materials (wood, reed, straw, bagasse) are pulped by a chemical process, wherein a difference is made between acidic (sulfite pulping) and alkaline (sulfate, soda, or organosolv [possibly organic solvents pulping]) methods.

The alkali pulp obtained in this manner is freed from the solid lignin by a common multistage bleaching method. This has taken place until now almost exclusively with chlorine-containing bleaching agents, such as elemental chlorine (C), chlorine dioxide (D), and hypochlorite (H). For the preparation of fully bleached alkali pulp, the following bleaching sequence, for example, was common:

(C) - (E) - (H) - (D) - (E) - (D)

(E) = extraction of the chlorolignins with sodium hydroxide.

To reduce the environment-polluting use of elemental chlorine, an alkaline oxygen bleaching (EO) was placed upstream and chlorine was extensively replaced by chlorine dioxide, wherein one arrived at the following bleaching sequence:

(EO) - (C/D) - (E) - (D) - (E) - (D)

A complete replacement of chlorine-containing bleaching agents by oxygen, hydrogen peroxide, or ozone was limited until now to laboratory experiments and led only either to semibleached

pulps with a brightness of 70 to 75 or, to a very great destruction of the cellulose fibers.

The goal of the invention under consideration was therefore to develop a method for the chlorine-free bleaching and delignification of alkali pulp, which does not exhibit the aforementioned disadvantages of the state of the art, but instead facilitates the preparation of fully bleached pulps with low technical expenditure and without using chlorine-containing treatment agents.

This goal was attained in accordance with the invention by the fact that the sulfate pulp was subjected to a bleaching sequence consisting of the following stages:

(A) - (C) - (A) - (B) - (B)

wherein (A) = treatment with an aqueous solution of an organic per-acid, (B) = bleaching with an alkaline, aqueous peroxide solution, perhaps activated by cyanamide or cyanamide salts, and (C) = extraction of the lignin components with an alkaline aqueous solution.

Surprisingly, it was namely shown that one arrives, in this manner, at a fully bleached alkali pulp with relatively few bleaching stages and without using chlorine-containing chemicals.

With the method in accordance with the invention under consideration, nonbleached alkali pulp, or alkali pulp that is prebleached, for example, by oxygen and/or hydrogen peroxide and/or ozone, is used as a starting substance; its brightness is approximately 20 to 40%, and its kappa values normally lie between 15 and 40. Such an alkali pulp is subjected, in accordance to the invention, to a bleaching sequence consisting of 5 stages.

The first stage comprises a treatment of the alkali pulp with an aqueous solution of an organic per-acid. In principle, all aliphatic and aromatic peroxocarboxylic acids can be used as the organic per-acids. It is recommended, however, to turn to the use of performic acid or peracetic acid for economic reasons and because of their good solubility, wherein peracetic acid is regarded as particularly preferred. Instead of peracetic acid, it is also possible to use a mixture of an aqueous hydrogen peroxide solution and acetic acid, wherein to establish the chemical equilibrium, this solution is stored at 0-80°C for 1-12 h, perhaps with the addition of a mineral acid.

The quantity of the aqueous solution of the organic per-acids used in stage (A) can be varied within broad limits, but it has proven to be particularly advantageous to use the per-acids in such a quantity that the active H_2O_2 is present at 0.1 to 3 wt%, based on the dry weight of the pulp, wherein the active H_2O_2 is determined by iodometric titration. If one turns to the use of a mixture of H_2O_2 and acetic acid, the molar ratio between acetic acid and H_2O_2 should be at least 1:1, and the acetic acid content should be 0.2-500 wt%, based on the dry weight of the pulp. Bleaching stage (A) is preferably carried out in an acidic milieu with a pH value of 1 to 7, wherein to establish the pH value, the usual acids or salts can be used. The organic per-acid may also contain stabilizers in the form of heavy-metal-complexing chelating agents, such as EDTA or DTPA. The preferred temperature range in stage (A) is 30 to 95°C, in particular 50 to 80°C, depending on the type and pretreatment of the pulp, wherein treatment times of 0.5-8 h are usually required. The pulp

consistency should preferably be established at 5 to 30 wt% in stage (A).

Following this bleaching stage (A), the dissolved lignin components are extracted with an alkaline aqueous solution in the second stage of the method in accordance with the invention, wherein one can turn to the use of the usual alkaline-reacting bases, such as hydroxides or carbonates of an alkali or alkaline earth metal. For economic reasons, however, sodium hydroxide is preferably used as the alkaline aqueous solution, wherein the NaOH content is in particular 0.1 to 5 wt%, based on the dry weight of the pulp. This extraction step (C) is preferably carried out at a temperature of 20 to 95°C; the treatment time is normally 0.2-4 h.

In the third stage of the method in accordance with the invention, the alkali pulp is subjected to a further bleaching stage (A)--that is, to a treatment with an aqueous solution of an organic per-acid, as already described above.

This bleaching stage (A) is followed in the fourth stage of the method in accordance with the invention by a bleaching with an alkaline, aqueous peroxide solution, perhaps activated by cyanamide or cyanamide salts. The H_2O_2 content in stage (B) is preferably 0.1 to 3 wt%, based on the dry weight of the pulp, whereas the cyanamide content of the activating cyanamide derivatives is between 0.1 and 2 wt%, also based on the dry weight of the pulp. Instead of cyanamide, its salts, such as the alkaline-reacting salts, sodium hydrogen cyanamide, calcium cyanamide, or magnesium cyanamide, can also be used.

Stabilizers, such as water glass or complexing agents (Na-EDTA), and aluminum or salts of the alkaline earth metals, can also be added in the usual amounts to the bleaching solution for stage (B). The pH of the bleaching solution for stage (B) should, as a rule, be 9 to 12, wherein the establishing of the pH takes place with the usual known alkaline-reacting substances, such as NaOH. The solids concentrations in bleaching stage (B) can also be varied within broad limits, wherein solids concentrations of 5 to 30 wt%, in particular 7 to 20 wt%, are regarded as preferable. The temperatures in bleaching stage (B) are preferably implemented at temperatures of 30 to 95°C, in particular 55 to 80°C, depending on the type of pulp and the desired brightness, wherein treatment times of 1-8 h are usually required.

Finally, in the fifth stage of the method in accordance with the invention, the alkali pulp is still subjected to a final treatment with an alkaline peroxide solution, which can perhaps be activated, as already described, by cyanamide or cyanamide salts. After this five-stage bleaching sequence, in accordance with the invention, an alkali pulp is obtained, whose brightness lies between 85 and 92% and which exhibits a kappa value of 0.5-2.5.

The following examples should explain the invention in more detail.

Examples

All bleaching stages were carried out in polyethylene bags. The bleaching solution indicated in the examples was worked into

the weighed pulp samples, then the samples were treated in a water bath in accordance with the indicated conditions. Subsequently, the pulp was washed.

Determinations

Brightness:

Standard white sheets were formed from the washed pulp with a sheet-making apparatus (Rapid Koethen); the brightness was determined in % according to the ISO-Norm 2470 with a measuring apparatus, Elrepho 2000 (Datacolor).

Kappa number:

The determination of this coefficient, which is a measure of the lignin content in the pulp, was carried out according to ISO-Norm 302.

Viscosity:

The determination of the viscosity was carried out in accordance with SCAN-C15:62. The value was given in dm^3/kg .

Bleaching sequences:

Were abbreviated in the following manner: EO: extraction supported with oxygen.

Example 1

Preparation of the aqueous peracetic acid solution for bleaching stage (A)

75 g of glacial acetic acid are mixed with 2 drops of concentrated sulfuric acid. Subsequently, 25 g of a 30% hydrogen

peroxide solution are carefully added to this solution. After standing for several hours at room temperature, the peracetic acid solution is ready to use.

Example 2

Spruce sulfate pulp, after EO pretreatment, with a kappa value of 18.3; a brightness of 33%, and a viscosity of 979.5, was subjected to the following bleaching sequence:

a) Stage (A):

Quantity of material: 398.4 g of (= 100 g of bone-dry)

Bleaching solution: 601.6 g of solution, which contains 40 g of peracetic acid solution from Example 1

Bleaching temperature: 75°C

Bleaching time: 180 min

b) Stage (C):

Quantity of material: 424.6 g of (= 85 g of bone-dry)

Bleaching solution: 425.4 g of solution, which contains 2.125 g of NaOH

Bleaching temperature: 80°C

Bleaching time: 90 min

c) Stage (A):

Quantity of material: 406.7 g of (= 85 g of bone-dry)

Bleaching solution: 443.3 g of solution, which contains 34 g of peracetic acid solution from Example 1

Bleaching temperature: 75°C

Bleaching time: 180 min

d) Stage (B):

Quantity of material: 79.4 g of (= 20 g of bone-dry)

Bleaching solution: 120.6 g of solution, which contains 0.6 g of H_2O_2 , 0.5 g of NaOH, and 0.1 g of cyanamide

Bleaching temperature: 75°C

Bleaching time: 180 min

e) Stage (B):

Quantity of material: 60.0 g of (= 15 g of bone-dry)

Bleaching solution: 90.0 g of solution, which contains 0.45 g of H_2O , 0.375 g of NaOH, and 0.075 g of cyanamide

Bleaching temperature: 75°C

Bleaching time: 180 min

A pulp with kappa 1.0, 89.5% brightness, and 743.4 viscosity was obtained.

Example 3

Spruce sulfate pulp, corresponding to the bleaching sequence (A) - (C) - (A), in accordance with Example 2 c), was subjected to the following treatment stages:

d) Stage (B):

Quantity of material: 79.4 g of (= 20 g of bone-dry)

Bleaching solution: 120.6 g of solution, which contains 0.6 g of H_2O_2 , and 0.5 g of NaOH

Bleaching temperature: 75°C

Bleaching time: 180 min